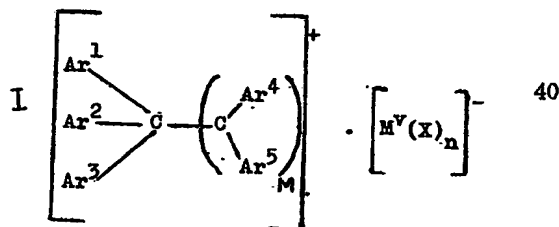# PATENT SPECIFICATION

COMPLETE SPECIFICATION

Oxymethylene Polymer Production

We, CELANESE CORPORATION, of 522 Fifth Avenue, New York 36, State of New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of oxymethylene polymers.

Oxymethylene polymers, including normally solid polymers of high molecular weight useful as moulding materials, can be made by polymerising formaldehyde or trioxane or other source of oxymethylene units, or by copolymerising such a compound with one or more other monomers. Many different catalysts can be used to assist these polymerisations including a large variety of halogen compounds, boron fluoride and its co-ordination complexes being of outstanding usefulness especially for polymerising or co-polymerising trioxane. The present invention is concerned with a new group of halogen-containing catalysts for use in oxymethylene polymer production, which catalysts are effective in very small proportions and very effective even in copolymerisations which are otherwise difficult to carry out with the efficiency needed for a commercial operation.

According to the invention an oxymethylene polymer is made by polymerising trioxane, or by copolymerising sufficient trioxane with one or more comonomers to form a copolymer containing at least 40 mole per cent of oxymethylene groups, in the presence as catalyst of a compound of the formula

$$I \quad \left[\begin{matrix} Ar^1 \\ Ar^2 \\ Ar^3 \end{matrix} \Big\rangle C \!-\!\! \left(C \Big\langle \begin{matrix} Ar^4 \\ Ar^5 \end{matrix} \right)_{m} \!\!\! M \right]^{+} \cdot \left[M^v(X)_n \right]^{-}$$

wherein Ar^1, Ar^2, Ar^3, Ar^4 and Ar^5 are the same or different aryl radicals, m is either zero or 1, M is an element as defined below, v is the valency of the element M, n equals v plus 1 and X is a halogen atom and is a chlorine, bromine or iodine atom when M is antimony.
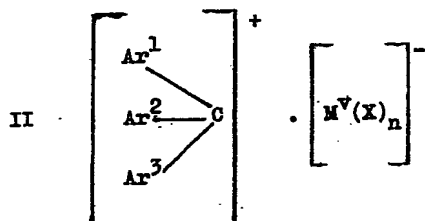
In the new catalysts the element M is one of the following elements which are listed in order of valency against the corresponding formula of the group $[M^v(X)_n]^-$:—

MX_2^{-1}	Au^{+1} and Ag^{+1}
MX_3^{-1}	Cu^{+2}, Zn^{+2}, Cd^{+2} and Hg^{+2}
MX_4^{-1}	Au^{+3}, Fe^{+3}, Cu^{+3}, Al^{+3}, Ga^{+3}, Sb^{+3}, In^{+3}, Tl^{+3}, Sc^{+3}, Y^{+3}, La^{+3}, Bi^{+3} and V^{+3}
MX_5^{-1}	Sn^{+4}, Zr^{+4} and Hf^{+4}
MX_6^{-1}	P^{+5}, Sb^{+5}, Bi^{+5}, V^{+5}, Nb^{+5} and Ta^{+5}

The halogen in the catalysts is preferably chlorine or fluorine.

Examples of aryl radicals which the Ar radicals may represent are phenyl, biphenylyl, naphthyl, anthracyl, phenylnaphthyl, phenylanthracyl and binaphthylyl, phenyl being preferred. Preferably, m is zero so that the compound may be represented by the formula

$$
\text{II} \qquad
\begin{bmatrix}
\text{Ar}^1 \\
\text{Ar}^2 \\!-\!\!\text{C} \\
\text{Ar}^3
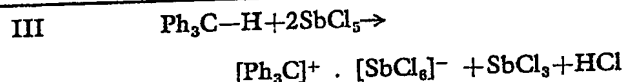\end{bmatrix}^+ \cdot \; \left[\text{M}^{\text{V}}(\text{X})_n \right]^-
$$

The element which M represents is preferably phosphorus, antimony or bismuth and, of these, antimony is preferred. Triphenylmethyl antimony hexachloride (TAHC) has been found to be an especially useful catalyst.

Illustrative examples of other compounds which can be used, in addition to triphenylmethyl antimony hexachloride, are the following: —

Triphenylmethyl antimony hexabromide and hexaiodide

Pentaphenylethyl antimony hexachloride, -bromide and -iodide

Triphenylmethyl phosphorus hexachloride

Pentaphenylethyl phosphorus hexachloride

Triphenylmethyl antimony tetrachloride

Pentaphenylethyl antimony tetrachloride

Triphenylmethyl bismuth tetrachloride

Pentaphenylethyl bismuth tetrachloride

Tris(biphenylyl)methyl antimony hexachloride

Trinaphthylmethyl phosphorus hexabromide

(Monophenyl)(dinaphthyl)methyl antimony tetrachloride

Mono-(biphenylyl)(diphenyl)methyl bismuth tetrachloride

The compounds which are used as polymerisation catalysts according to the invention can be prepared by, for example, one or the other of the general procedures which are exemplified by the following simplified equations which are given, by way of example, with reference to the preparation of triphenylmethyl antimony hexachloride and wherein "Ph" represents the phenyl radical.

The first procedure illustrates the technique used by Holmes and Pettit, *Journal of Organic Chemistry*, 28, 1695—96 (1963): —

III $\text{Ph}_3\text{C}-\text{H} + 2\text{SbCl}_5 \rightarrow$

$[\text{Ph}_3\text{C}]^+ \cdot [\text{SbCl}_6]^- + \text{SbCl}_3 + \text{HCl}$

The second procedure can be illustrated as follows: —

IV $\text{Ph}_3\text{C}-\text{Cl} + \text{SbCl}_5 \rightarrow$

$[\text{Ph}_3\text{C}]^+ \cdot [\text{SbCl}_6]^-$
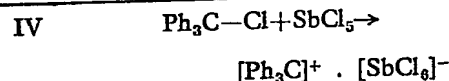
Details of this procedure with particular reference to the preparation of TAHC are given below in Example 1.

The oxymethylene polymer made by the process of the invention may be a homopolymer or an oxymethylene copolymer. The latter may be, for example, a copolymer having a structure comprising recurring units consisting of (A)—OCH_2— groups interspersed with (B) groups represented by the general formula

$$-\text{O}-\text{CR}_1\text{R}_2-\text{CR}_1\text{R}_2-(\text{R}_3)_n-$$
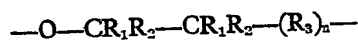
wherein each R_1 and R_2 is selected from the group consisting of hydrogen, lower alkyl and halogen-substituted lower alkyl radicals, each R_3 is selected from the group consisting of methylene, oxymethylene, lower alkyl and haloalkyl - substituted methylene, and lower alkyl and haloalkyl-substituted oxymethylene radicals, and n is zero or an integer from 1 to 3, inclusive. Preferably, each lower alkyl radical has either one or two carbon atoms, and the —OCH_2— units of (A) constitute from 85% to 99.9% of the recurring units. The units of (B) may be incorporated into the copolymer by the opening of the ring of a cyclic ether having adjacent carbon atoms by the breaking of an oxygen-to-carbon linkage.

Oxymethylene copolymers of the kind described above can be prepared by copolymerising trioxane and from 0.1 to 15 mole per cent of a cyclic ether having at least two adjacent carbon atoms.

Among the cyclic ethers that may be employed in preparing an oxymethylene copolymer are ethylene oxide, 1,3 - dioxolane, 1,4-dioxane, trimethylene oxide, tetramethylene oxide (tetrahydrofuran), pentamethylene oxide, 1,2-propylene oxide, 1,2-butylene oxide, 1,3-

butylene oxide and 2,2-di(chloromethyl)-1,3-propylene oxide.

Examples of other compounds which may be copolymerised with trioxane in making the copolymers are 1,3-dioxane, 1,3,5-trioxepane, beta - propiolactone, gamma - butyrolactone, neopentyl formal, pentaerythritol diformal, paraldehyde (2,4,6 - trimethyl-1,3,5-trioxane), butadiene monoxide, ethylene glycol, diethylene glycol, 1,3-butylene glycol and propylene glycol.

Oxymethylene copolymers containing at least 40 mole per cent of recurring oxymethylene groups can best be obtained by the use of at least 44.4 weight per cent of trioxane in the polymerisable mixture of monomers. Preferably the proportions of comonomers, e.g. trioxane and a cyclic ether containing adjacent carbon atoms, are so proportioned that the oxymethylene copolymers contain from 60 mole per cent to 99.9 mole per cent of recurring oxymethylene groups and from 0.1 mole per cent to 40 mole per cent of —OR— groups, where R is an alkylene group or substituted alkylene group containing at least two carbon atoms, and especially from 70 to 99.6 mole per cent of oxymethylene groups and 30 to 0.4 mole per cent of such —OR— groups, the most useful copolymers having from 85 to 99.6 mole per cent of —OR— groups in which R is —CH₂—CH₂—.

Various other binary and also ternary and higher multi-component oxymethylene polymers may be prepared with the aid of the catalyst of the invention, including copolymers of the kind disclosed in Specification No. 1,026,777.

The amount of the polymerisation catalyst employed may be considerably varied. Usually it is employed in a molar amount within the range of from 1 x 10⁻⁵ mole per cent to 100 x 10⁻³ mole per cent, and preferably from 5 x 10⁻⁵ mole per cent to 15 x 10⁻³ mole per cent, based on the molar amount of monomeric material charged to the polymerisation zone. A larger amount of catalyst is required in a continuous operation than in a semi-continuous or batch process.

The monomer or plurality of monomers charged to the reaction zone is preferably anhydrous or substantially anhydrous. A small amount of moisture, such as may be present in a commercial grade of reactant material or that may be introduced by contact of the feed material charged to the reactor with atmospheric air will not prevent polymerisation, but should be removed for optimum results.

In one method of carrying out the polymerisation trioxane, alone or with one or more other monomers copolymerisable therewith, are blended with the catalyst which may be dissolved in a solvent, e.g. dry ethylene chloride, or slurried in a non-solvent, e.g. dry cyclohexane. The blend is then permitted to react in a sealed reaction zone while being subjected to a constant shearing action. The temperature in the reaction zone may vary from, for example, 0°C. to 115°C., and the period of reaction from, for instance, 5 minutes to 72 hours. The polymerisation reaction may be effected under pressures ranging from sub-atmospheric to 100 atmospheres or more.

Upon completion of the polymerisation reaction it is desirable to neutralize the activity of the polymerisation catalyst since prolonged contact with the catalyst tends to degrade the polymer. Various methods of neutralizing the activity of the catalyst may be employed, a convenient method comprising subjecting the reaction mass to a wash with an aqueous wash liquid. The initial contact of the reaction mass with an aqueous wash, which can be water alone, immediately neutralizes or deactivates the catalyst and renders it ineffective for both polymerisation and degradation reactions. On removal from the solid oxymethylene polymer the aqueous wash liquid carries with it unreacted trioxane in aqueous solution.

Instead of using water alone, the aqueous wash liquid may comprise an aqueous solution of an inorganic basic salt, such as sodium carbonate, or a mixture of water and a water-soluble organic solvent, e.g. an alcohol or ketone of low carbon content, or the wash liquid may contain an aliphatic amine, e.g. triethylamine or tri-n-butylamine, in stoichiometric excess over the amount of free catalyst in the polymeric product.

The washing step may be carried out at any temperature at which the wash liquid may be maintained in the liquid phase, aqueous wash liquids preferably being used at a temperature of from 80° to 100°C.

In general, the techniques useful in making the polymers, in quenching or neutralizing the catalyst in the product and for effecting stabilisation of the polymer are the same as when the polymerisation catalyst is a conventional catalyst of the boron trifluoride type. The polymers may be end-capped by acylation or esterification after polymerisation or during polymerisation by the use of selected chain-transfer agents, detailed information concerning such end-capping technique being described in the article by Kern et al in *Angewandte Chemie, 73, 6*, pages 177 to 186, of March 21, 1961.

The following examples, in which all parts and percentages are by weight unless otherwise stated, illustrate the invention.

EXAMPLES 1A TO 1F

The catalyst, triphenylmethyl antimony hexachloride (TAHC), was prepared as follows:—

In a dry-box, constantly purged with dry nitrogen, 0.1 mole (27.9 g.) of triphenylmethyl chloride was dissolved in 200 ml. of dry benzene (distilled over metallic sodium) contained in a 500 ml. glass-stoppered Erlenmeyer flask. By means of a clean, dry hypodermic syringe 0.11 mole (32.9 g.) of antimony pentachloride

was added to the solution while stirring vigorously. A reddish brown precipitate formed and continued to form throughout the addition of the antimony pentachloride accompanied by a slight temperature rise.

Continuing to work in the dry-box, there was then added 300 ml. dry pentane, followed by vigorous stirring and then decantation of liquids present. This procedure was repeated four times and followed by two washes of residual solids with dry diethyl ether. Finally, the flask was stoppered and placed quickly in a vacuum oven maintained at 50°C. A purge of dry nitrogen was started, the stopper removed from the flask, the oven door closed and vacuum applied. Drying was continued for 16 hours. The dry powder, dark orange in colour, was then transferred to clean, dry jars and stored in a vacuum desiccator.

Further purification was performed in the dry-box on one-half of the catalyst in the following manner:

The catalyst was dissolved in dry ethylene dichloride and precipitated by the addition of dry pentane. The mother liquor was decanted. The procedure was repeated six times. Removal of the solvents was effected in the manner described above. This further-purified catalyst likewise was stored in clean, dry jars placed in a vacuum desiccator.

In Examples 1A to 1F the polymerisations were effected in sealed, tared, glass tubes (i.e. so-called "bulk" polymerisations). The general procedure was as follows:

The glass tubes, of 125 ml. capacity, were closed with metal bottle caps pierced by a small central hole and provided with neoprene-Teflon gaskets. ("Teflon" is a Registered Trade Mark). The charged tubes were mounted on a rotating frame submerged in a silicone oil bath maintained at 60°C.

The trioxane used was of a commercial grade of purity that would yield polymer having a 1X melt index of 0.70. In all but one of the Examples the monomers used were 100 grams of trioxane and 2 grams of ethylene oxide but in Example 1C, there was used 3.2 grams of 1,3-dioxolane as a comonomer instead of 2.0 grams of ethylene oxide but the molar amounts were the same. When ethylene oxide was used it was fed in by means of a cold dry syringe through the hole in the cap on the tube. The reaction temperature was 63°C. Quenching of the polymer to deactivate the catalyst was effected by quickly removing the reaction mass from the reactor tube into a quench bath of acetone containing 0.1% tri-n-propylamine, followed by washing twice with acetone, and drying for 16 hours in vacuo at 60°C. The results obtained are set out in Table I.

TABLE I

Summary of Conditions and Results for Tube Copolymerizations of
Trioxane and Ethylene Oxide or 1,3-Dioxolane Using TAHC as Catalyst

Example No.	1—A	1—B	1—C	1—D	1—E	1—F
Catalyst, Moles $\times 10^{-5}$						
TAHC	36.8(a)	7.37(a)	7.37(a)	3.50(a)	7.10(a)	7.30(b)
React. Time, Min. (sec) To Turbidity	(15)	3.7	—	13.0	5.9	6.1
To Cream	—	3.9	—	15.3	6.4	6.6
To Solid	(25)	4.3	(10)	16.1	7.1	6.9
To Quench	40	30	30	50	50	40
Properties						
Crude Yield, %	93.3	86.6	87.6	44.3	64.1	80.4
Melt Stab. Loss, % (c)	50.1	16.0	28.4	—	15.6	19 7(d)
Overall Yield, %	44.7	72.7	62.7	—	54.1	64.6(d)
I. V. (e)	0.20	0.44	0.30	0.76	0.53	0.55

Footnotes to Table I

(a) The catalyst was added in the form of a solution of TAHC dissolved in 5 g. of ethylene chloride.

(b) The catalyst was added in the form of a slurry of TAHC in cyclohexane in which it is insoluble.

(c) The Melt Stabilization Loss, which is sometimes designated as Melt Hydrolysis Stabilization Loss, is determined as follows:

An accurately weighed sample of reactor polymer, after addition of antioxidants, is fed to a Plastograph chamber maintained at 190°C. under nitrogen for 45—60 minutes at which time the Plastograph torque becomes constant and melt degassing or stabilization is finished. The remaining stable polymer is weighed, and the percentage loss of unstable end groups is calculated as percentage loss.

Melt stabilization and solution hydrolysis stabilization (see footnote d) accomplish the same result by the individual techniques, i.e., remove unstable end groups from the crude reactor polymer. The values for % weight loss should be the same or nearly the same when determined by either technique.

(d) The crude copolymer was solution-hydrolysis stabilized by treatment with 1 g. NaOH dissolved in a 60/40 by weight mixture of methanol and water at 160°C.

(e) I.V. = inherent viscosity measured at 60°C. in 0.1 weight percent solution in p-chlorophenol containing 2 weight percent of alpha-pinene.

From the data in Table I showing the concentration of the initiator (catalyst) employed in Examples 1-A, 1-B, 1-D and 1-E in producing copolymers of trioxane and ethylene oxide, it will be noted that there is a general overall trend to copolymer of higher molecular weight and decreasing copolymer yields at decreasing concentrations of TAHC catalyst.

EXAMPLES 2A TO 2C

Examples 2A and 2C illustrate the solution polymerization of trioxane and ethylene oxide in anhydrous benzene using varying amounts of TAHC as a catalyst and under varying temperature and other conditions of reaction. For comparison Example 2B was carried out using a BF$_3$. di-n-butyl etherate complex as a catalyst.

The apparatus employed and general procedure were as follows:

A one-liter, 3-neck, round-bottom flask was adapted with a stirring shaft and bearing, reflux condenser and drying tube. The complete, clean apparatus was dried in a circulating air oven at 115°C. The entire apparatus was then removed and clamped temporarily on a ring stand. To the flask was quickly charged 250 g. of molten trioxane and 250 g. of anhydrous benzene. (The benzene previously had been refluxed for 24 hours over metallic sodium and fractionated through a 2-foot, packed, vacuum-jacketed column. When required, 250 g. cuts from the refluxing mass were collected in clean, dry tightly stoppered bottles for transfer to the reaction flasks.) After charging the molten trioxane and dry benzene to the flask, 5 g. of ethylene oxide was added by

means of a cold, dry syringe. Then the complete assembly was clamped into position in a constant-temperature bath and an electrical stirring motor was attached to the stirring shaft. After temperature equilibrium in the flask had been attained, the TAHC was added by means of a funnel as a slurry in dry benzene. The BF$_3$. etherate complex was charged by means of a hypodermic syringe.

At the end of the reaction period, the individual TAHC - catalyzed copolymers were neutralized by treatment with a methanol solution of 1 g. KOH in 100 ml. methanol, further washed with acetone, and then dried under vacuum at 60°C. The copolymer prepared with BF$_3$ as a catalyst was neutralized with tri-n-butylamine in acetone, further washed with acetone and then dried in the same manner as the TAHC-catalyzed copolymers.

The results are summarized in Table II. The trioxane was from the same lot as that used in Example 1, and was melted and filtered before use. Solution polymerizations were made at approximately 50% weight concentrations of the monomers (trioxane and ethylene oxide) in either dry cyclohexane (Example 2-A) or in benzene (Examples 2-B and 2-C) that had been distilled and refluxed over sodium metal for 24 hours as described above.

In Example 2-A the catalyst was TAHC, and the reaction temperature was approximately 63°C. Using initially 1.11 x 10^{-4} moles of TAHC (equivalent to 30 p.p.m. BF$_3$) no reaction occurred after one-half hour. Subsequent additions of catalyst were made until 7.73 x 10^{-4} moles of TAHC (equivalent to

210 p.p.m. BF₃) had been added before turbidity and subsequent polymerization occurred. The yield of crude polymer was about 27%.

Examples 2-B and 2-C were paired runs wherein BF₃-etherate complex was used in 2-B and TAHC in 2-C as the catalysts. Both runs were made in dry benzene as the solvent, and the polymerizations were initiated with equimolar concentrations of BF₃ and TAHC. The concentration was the equivalent of 100 p.p.m. BF₃ based on trioxane. In both runs additional catalyst was added when no reaction had occurred after a reasonable length of time. Finally, the temperature was quickly raised from about 41°C. to 56°C. Very little copolymer (about 1.2%) resulted from the BF₃-catalyzed polymerization after a total of 5.25 hours. In marked contrast, the TAHC-catalyzed polymerization provided a yield of 21.9% of copolymer after a total reaction time of only 3 hours.

TABLE II

Summary of Conditions and Results for Solution Copolymerizations of Trioxane and Ethylene Oxide Using BF₃-Etherate Complex and TAHC as Catalysts

Example No.	2-A	2-B	2-C
Conditions			
Trioxane, g.	250	250	250
Benzene, g.	—	250	250
Cyclohexane, g.	250	—	—
Ethylene Oxide, g.	5	5	5
Catalyst, Moles $\times 10^{-4}$ BF₃(a) Initial	—	3.68(c)	—
TAHC Initial	1.11(b)	—	3.68(d)
BF₃ (Total)	—	7.36(c)	—
TAHC (Total)	7.73(b)	—	7.36(d)
Reaction Temp., °C	62—64	41—41.5(c) (Initial temperatures)	41.0(d)
Reaction Time, Hrs.	0.90	5.25	3.0
Properties			
Crude Polymer Yield, g. (%)	67.9 (27.2)	3.1 (1.2)	54.8 (21.9)
Melt Stab. Loss, %	42.4	(e)	27.0
Overall Yield, %	14.6	(e)	16.0

Footnotes to Table II

(a) BF$_3$ was charged as BF$_3$.di-n-butyl etherate complex. However, the amount shown is that of uncomplexed BF$_3$. One hundred (100) p.p.m. BF$_3$ (based on 250 g. trioxane) corresponds to 3.68×10^{-4} moles.

(b) The amount of TAHC initially added was 1.11×10^{-4} moles. Additional catalyst was added at intervals until a total of 7.73×10^{-4} moles had been added.

(c) The amount of catalyst initially was 3.68×10^{-4} moles. An additional amount (3.68×10^{-4} moles) was added after 3.5 hours. After 4 hours the temperature was raised to 56°C. for an additional 1.25 hours, making the total reaction time 5.25 hours.

(d) The amount of catalyst initially added was 3.68×10^{-4} moles. After 1 hour the same amount of more catalyst was added. After an additional 1/2 hour the temperature was raised to 56°C. and held at that temperature for an additional 1.5 hours, making the total reaction time 3 hours.

(e) Insufficient copolymer to make this test.

EXAMPLE 3

This example illustrates the preparation of a copolymer of trioxane and tetrahydrofuran (tetramethylene oxide).

Into a clean, dry, 250-ml., round-bottom flask was collected 52.9 g. of tetrahydrofuran that had been refluxed over NaOH and metallic sodium for 48 hours. In the same flask was collected 51.4 g. of trioxane that had been similarly purified by refluxing over fresh sodium hydroxide pellets and small metallic sodium chunks while maintaining an atmosphere of dry, prepurified nitrogen in the flask so as to blanket the contents of the flask. The trioxane for copolymerization with the tetrahydrofuran was collected only after the head temperature of the flask had reached 114.5°C.

After the trioxane and tetrahydrofuran had been charged to the reaction flask, there was added thereto 0.2475 g. (4.28 x 10^{-4} mole) of TAHC catalyst. The sealed flask was allowed to stand for 72 hours at ambient temperature with occasional stirring. At the end of this period of time the reaction mass had become solid. The contents of the flask were repeatedly extracted with acetone in a Waring Blendor, filtered and dried.

A yield of 55.6 g. (53.5%) of acetone-insoluble copolymer with a melting point of 164°—165°C. resulted. All acetone washes were collected, and the acetone was removed therefrom under vacuum at ambient temperature. There was obtained a yield of 32.9 g. (31.6%) of acetone-soluble polymer, which was initially a viscous syrup at room temperature but crystallized to a solid (M.P. 36°—37°C.) on standing.

The conditions and the results, including some properties of the product, are summarized below.

Charge to Reactor	Grams	Weight %	Moles
Trioxane	51.4	49.28	
Tetrahydrofuran	52.9	50.72	
TAHC (catalyst)	0.2475		(4.3×10^{-4})
Reaction temperature, °C.		25	
Reaction Time, °C.		72	

	Acetone Insoluble Polymer	Acetone Soluble Polymer
Crude polymer yield	55/6 g. (53.3%)	32.9 g. (31.6%)
Melt stability loss, %(a)	12.8	—
Overall yield, %	47.0	—
Melting point, °C.	164—165(b)	36—37
Melt index (1X)	Very high	—

(a) After melt stabilization of the polymer as described in footnote (c) to Table I.

(b) The crystalline melting point was 160°—161°C.

That a true copolymer of trioxane and tetrahydrofuran had been obtained is evidenced by the following facts and observations.

Some of the acetone-insoluble polymer (M.P. 164°—165°C.) was acid hydrolyzed and all of the formaldehyde was flashed off. The residue that remained amounted to 22.4 weight percent of this polymer.

Some of the same polymer sample was acid hydrolyzed and the acid hydrolysate (not the residue) was examined for the presence of 1,4-butanediol (which would result from the ring opening of tetrahydrofuran as it entered the polymer molecule) by Gas Chromatographic (G.C.) analysis versus a standard 1,4-butanediol sample. No. 1,4-butanediol was found in the hydrolysate. Furthermore, no other peaks (other than those due to formaldehyde) were found in the G.C. curve for the hydrolysate.

Hence the acetone-insoluble polymer was a copolymer of 77.6 wt. % formaldehyde and 22.4 wt. % tetrahydrofuran, or 89.3 mole % formaldehyde and 10.7 mole % tetrahydrofuran.

It may also be mentioned that if only homopolymeric oxymethylene had been formed, the solution stabilization loss would have been 100%.

EXAMPLES 4 THROUGH 28

Essentially the same procedure was followed as described in the foregoing examples, in preparing other oxymethylene polymers (including homopolymer and binary and ternary polymers) from the following proportions of the specified monomer(s) with substantially the same results. The designated components in making the polymers, using triphenylmethyl antimony hexachloride as catalyst, are in parts by weight.

4. 100 trioxane
5. 100 trioxane and 1 ethylene oxide
6. 100 trioxane and 2 1,4-dioxane
7. 100 trioxane and 1.5 trimethylene oxide
8. 100 trioxane, 1 1,2-propylene oxide and 0.5 butadiene dioxide
9. 100 trioxane and 2 pentamethylene oxide
10. 100 trioxane and 1 1,2-butylene oxide
11. 100 trioxane and 2 1,3-butylene oxide
12. 100 trioxane, 2 ethylene oxide and 0.1 vinylcyclohexene dioxide
13. 100 trioxane and 2 tetrahydrofuran
14. 100 trioxane, 2 ethylene oxide and 2 tetrahydrofuran
15. 100 trioxane, 2 ethylene oxide and 0.1 diglycidyl ether of bisphenol A
16. 100 trioxane, 2 ethylene oxide and 0.5 diacetal of malonaldehyde and ethylene glycol
17. 100 trioxane, 16.8 1,3-dioxolane and 0.5 vinylcyclohexene dioxide
18. 100 trioxane, 2 ethylene oxide and 2 sorbitol triformal
19. 100 trioxane, 2.2 ethylene oxide and 0.5 pentaerythritol diformal
20. 100 trioxane, 3 ethylene oxide and 2 tetrahydrofuran
21. 100 trioxane, 2.1 ethylene oxide and 1.0 pentaerythritol diformal
22. 100 trioxane, 2 ethylene oxide and 0.5 vinylcyclohexene dioxide
23. 100 trioxane, 2 ethylene oxide and 0.5 butadiene dioxide
24. 100 trioxane, 2 ethylene oxide and 0.5 resorcinol diglycidyl ether
25. 100 trioxane, 12.6 1,3-dioxolane and 0.5 vinylcyclohexene dioxide
26. 100 trioxane, 2 ethylene oxide and 0.3 triepoxide of the triallyl ether of trimethylolpropane
27. 100 trioxane and 50 tetrahydrofuran
28. 100 trioxane, 25 ethylene oxide and 25 tetrahydrofuran

WHAT WE CLAIM IS:—

1. Process for the production of an oxymethylene polymer by polymerising trioxane, or by copolymerising sufficient trioxane with one or more comonomers to form a copolymer containing at least 40 mole per cent of oxymethylene groups, wherein the polymerisation is carried out in the presence as catalyst of a compound of the formula
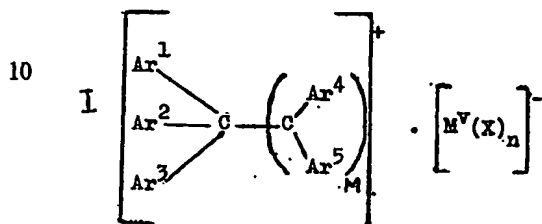
wherein Ar^1, Ar^2, Ar^3, Ar^4 and Ar^5 are the same or different aryl radicals, m is either zero or 1, M is an element as hereinbefore defined, v is the valency of the element M, n equals v plus 1 and X is a halogen atom and is a chlorine, bromine or iodine atom when M is antimony.

2. Process according to Claim 1, wherein the catalyst used is one containing three Ar radicals all of which are phenyl radicals.

3. Process according to Claim 1 or 2, wherein the catalyst used is one in which X is a chlorine or fluorine atom.

4. Process according to Claim 3, wherein the catalyst used is triphenylmethyl antimony hexachloride.

5. Process according to any of the preceding claims, wherein trioxane is copolymerised with a cyclic ether having adjacent carbon atoms.

6. Process according to Claim 5, wherein trioxane is copolymerised with one or more comonomers including ethylene oxide, tetrahydrofuran or 1,3-dioxolane.

7. Process according to any of the preceding Claims, wherein a plurality of comonomers including from 99.9 to 85 mole per cent of trioxane and from 0.1 to 15 mole per cent of a cyclic ether having adjacent carbon atoms are polymerised.

8. Process for the production of oxymethylene polymers according to Claim 1 and substantially as hereinbefore described.

9. Oxymethylene polymers, whenever produced by any of the processes claimed in the preceding Claims.

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